

Additional Trials & Tribulations in Synthesizing a Sulfide Standard

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Well-characterized sulfide reference materials that can serve as matrix-matched calibrants for *in-situ* trace element analyses via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) remain elusive. Here, we describe the creation of an in-house sulfide standard at NASA JSC that will be used to measure siderophile and chalcophile trace elements in low pressure experimental products, specifically pentlandite ($[\text{FeNi}]_9\text{S}_8$) and pyrrhotite ($[\text{FeNi}]_{1-x}\text{S}$), as well as natural sulfides in terrestrial and meteoritic mineral assemblages. Recent methods in creating a homogenous sulfide standard include pressed pellets, synthesized chips, or fused glass [e.g. 1-3]. Other studies, however, have had success in forming homogenous FeS standards via synthesis methods [e.g. 4-6]. We present a variation of the method described in [4], in which we create a pyrrhotite standard doped with a variety of trace elements (Zn, As, Se, Mo, Ru, Rh, Pd, Sn, Sb, Te, W, Os, Ir, Pt, Au) at ~10-40 ppm and Cu at ~200 ppm.

Sulfide compositions were constructed using Fe and Ni metal and elemental sulfur powders. Trace elements were added to elemental sulfur from Atomic Absorption Spectroscopy (AAS) elemental standards as either nitrate or chloride solutions to prevent oxidation of the metal powders. The dried sulfur mixture was mixed with Fe and Ni powders and mechanically mixed before two aliquots were placed in separate SiO_2 tubes. Each tube was held under vacuum for ~30 minutes, sealed under vacuum, and then heated at 800°C for 48 hours. Like [4], the synthesis products were composed of porous sulfide crystals. Major element analyses of both experimental aliquots, collected using an Electron Probe Microanalyser (EPMA), yield indistinguishable major element compositions (uncertainties in 2SE & 2RSE[%]), with an average of 57.90 ± 0.09 (0.16 %), 4.95 ± 0.03 (0.55 %), and 39.70 ± 0.14 (0.34 %), for Fe, Ni, and S, respectively. Trace element data were measured using a Photon Machines 193nm laser ablation system coupled to a Thermo-Scientific Element-XR ICP-MS. Spot sizes were limited to 50 μm due to the porous nature of the sulfide target material. Trace element abundances, normalized to Fe as an internal standard, were also found to be homogenous between the two aliquots, with weighted mean 2RSE (%) values of <3.0 for all trace elements.

Synthesized products were re-powdered and absolute concentrations measured via solution ICP-MS. Although the sulfide appears to be homogenous, sintering experiments will be performed to more closely match the standard density to natural sulfides and minimize differences in ablation behavior. Improved density also allows for higher sensitivity (i.e. more compact target material) and larger spot sizes or traverses, as void space is eliminated. Additional major and trace element analyses on the products of the sintering experiments will be undertaken.

References: [1] Wilson et al. (2002) *J. Anal. Atom. Spectrom.*, **17**(4), 406-409. [2] Onuk et al. (2017) *Geostand Geoanal Res.*, **41**(2), 263-272. [3] Ding et al. (2011) *Mineral Mag.*, **75**(2), 279-287. [4] Wohlgemuth-Ueberwasser et al. (2007) *Contrib Mineral Petr.*, **154**, 607-617. [5] Ballhaus & Sylvester (2000) *J Petrol.*, **41**(4), 545-561. [6] Barnes et al. (2006) *Contrib Mineral Petr.*, **152**, 187-200.